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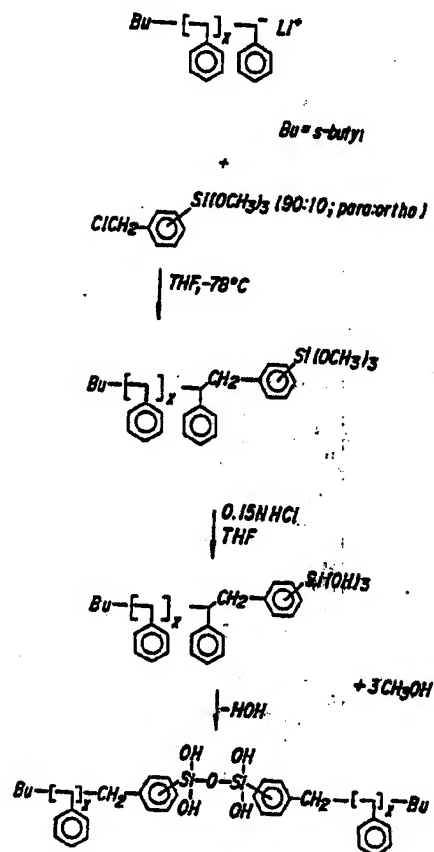
WORLD INTELLECTUAL PROPERTY ORGANIZATION
International Bureau

INTERNATIONAL APPLICATION PUBLISHED UNDER THE PATENT COOPERATION TREATY (PCT)

(51) International Patent Classification ⁵ : C08F 297/02, 8/42 C08G 81/02, C08C 19/44	A1	(11) International Publication Number: WO 90/09403 (43) International Publication Date: 23 August 1990 (23.08.90)
(21) International Application Number: PCT/US90/00760 (22) International Filing Date: 13 February 1990 (13.02.90) (30) Priority data: 311,555 16 February 1989 (16.02.89) US (60) Parent Application or Grant (63) Related by Continuation US 311,555 (CIP) Filed on 16 February 1989 (16.02.89) (71) Applicant (for all designated States except US): EASTMAN KODAK COMPANY [US/US]; 343 State Street, Ro- chester, NY 14650 (US).		(72) Inventors; and (75) Inventors/Applicants (for US only): LONG, Timothy, Ed- ward [US/US]; 29 Rosecroft Drive, Rochester, NY 14616 (US). TURNER, Sam, Richard [US/US]; 4 Woodstone Rise, Pittsford, NY 14534 (US). (74) Agent: LINN, Robert, A.; 343 State Street, Rochester, NY 14650 (US). (81) Designated States: AT (European patent), BE (European patent), CA, CH (European patent), DE (European pa- tent), DK (European patent), ES (European patent), FR (European patent), GB (European patent), IT (European patent), JP, LU (European patent), NL (European pa- tent), SE (European patent), US. Published With international search report.

(54) Title: SILYL TERMINATED POLYMERS**(57) Abstract**

Alkoxysilyl terminated polymers are prepared with narrow molecular weight distributions, predictable molecular weights, and high functionality. The functionality is controlled by employing either a monofunctional ($f=1$) or difunctional ($f=2$) initiator. The endcapped materials can be condensed under acidic conditions. Monofunctional polymers are soluble after condensation and amenable to SEC and ^{29}Si NMR analysis. On the other hand, difunctional condensates can be insoluble in common organic solvents. Monofunctional products exhibit extraordinary condensation behavior. The narrow molecular weight distribution of the precursors is preserved after condensation, and the extent of growth is a function of the method of preparation. The monofunctionalized products can serve as stable precursors for the preparation of soluble, branched polymers.



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SILYL TERMINATED POLYMERSTechnical Field

This invention relates to anionic living
5 polymers which have been terminated with a
silicon-containing group and subsequently linked
together by a condensation reaction. The condensed
products have a narrow molecular weight distribution.
The degree or extent of processing, according to the
10 disclosed process, determines the size and structural
characteristics of the condensed polymers provided by
this invention.

Background of the Invention

15 It is known in the art that a lithium-
terminated polymer can be reacted with a compound
having multi-functional active sites which are capable
of reacting with the Li-C bond in the polymer. In the
art, such a reaction is used to prepare linear and
20 radical polymers. For such polymers, the
multi-functional coupling agent becomes a nucleus for
the resulting structure. From the nucleus, polymeric
branches radiate.

Silanes, siloxanes, and certain silicic
25 coupling agents have been used in the art. In general,
the processes of the art comprise using multi-step
procedures, and/or an excess of the lithium-terminated
polymer to make sure that all, or substantially all, of
the reactive sites of the coupling reagent enter into
30 the coupling reaction.

Multi-step preparative processes are tedious,
time-consuming, and comparatively expensive.
Furthermore, when an excess of starting polymer is
employed, the excess must be removed from the resulting
35 product. Frequently, extraction or a similar technique
is used to separate the excess reactant from the
product. Such separation techniques are expensive.

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For a brief discussion of prior art in this area, reference is made to U.S. 4,185,042.

Reference is also made to U.S. 4,618,650. In contrast to other prior art, it teaches that it is
5 necessary to use a stoichiometrically perfect relationship between SiCl_4 and a lithium-terminated polymer for star polymer formation to occur. The patent teaches that if more than a stoichiometric amount of SiCl_4 is used, PSiCl_3 is formed ($P =$ a
10 living polymer) and these $-\text{SiCl}_3$ terminated chains do not react with each other to become cross-linked. Achievement of a stoichiometrically perfect reactant ratio is very difficult to obtain, especially on an industrial scale.

15 U.S. 4,618,650 also discloses termination of a "living" polymer carbanion using tetrachlorosilane (in excess) to generate a trichlorosilyl-terminated polymer. In a second step, a tertiary alcohol such as tert-butanol is reacted to form a tributoxysilyl-
20 terminated intermediate. Finally the endcapped intermediate is heated at 100°C for 16 hours or so to obtain a branched polymer. These products can be huge polymeric networks that can theoretically contain an infinite number of polymer chains (see column 2, lines
25 26-28).

It is also known in the art that polystyrene with pendant silane groups can be grafted onto silica; Laible et al, Advances in Colloid and Interface Science
13, (1980) 65-99. The products are a surface-modified
30 silica.

The complexity of prior art processes for forming stars is illustrated by Fetters et al, Macromolecules 1980, 13, 191-193. To prepare an 18
arms star, it was first necessary to prepare a linking
35 agent with 18 chlorine atoms, and then conduct a prolonged polymerization reaction. It would be desirable to provide uncomplicated processes that yield

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well-defined stellate polymers of narrow molecular weight distribution.

In accordance with one embodiment of this invention, there is provided a process for the
5 preparation of a polymer having a narrow molecular weight distribution, said process comprising:

(i) reacting a metal terminated living anionic polymer with a halotrialkoxysilane wherein each
10 alkoxy group has from one to about four carbon atoms and to form a polymer endcapped with a trialkoxysilyl group, said process being conducted in the presence of an inert organic solvent for said metal terminated polymer,

(ii) subjecting the trialkoxysilyl terminated
15 polymer thereby produced to a hydrolysis/condensation reaction by contacting water with said trialkoxysilyl terminated polymer in the presence of a catalytic amount of an acidic or basic catalyst, and an inert organic solvent,

(iii) heating the precursor product thereby
20 produced at a temperature and for a time sufficient to form a condensed polymer.

In accordance with another embodiment of this invention, there is provided a polymer having a MWD
25 within the range of from about 1.15 to about 1.70, said polymer being selected from unifunctional and difunctional chains endcapped with a silicon-containing functionalizing group, said group being divalent and bonded through one valence to an end of said chain, and
30 though the other valence to a silicon atom, which is bonded to three oxygen atoms, each of said oxygen atoms being bonded to a moiety selected from the hydrogen radical, lower alkyl radicals and another silicon atom in another of said endcapped chains, such that the
35 ratio of the number of silicon atoms bonded to one other silicon atom via an oxygen bridge, to the number of silicon atoms bonded to two other silicon atoms via oxygen bridges is 2:1 or lower.

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In contrast to the prior art, the polymers of this invention are not merely surface-treated inorganic substances. Moreover, the materials of this invention are well-defined stellate polymers of narrow molecular weight distribution (MWD). They have solubility characteristics which are completely different from the networks of U.S. 4,618,650. Furthermore, the narrow molecular weight distribution and the nucleus from which the polymer arms radiate completely differentiate the polymers of this invention from prior art materials.

The process of this invention does not require the procedures used in the prior art to achieve good coupling efficiency. Thus the process of this invention does not require the expensive steps resorted to by prior workers and mentioned above.

Furthermore, the process of this invention comprises a well-controlled, facile method for the formation of well-defined stellate polymers having a discrete number of polymer chains per molecule. The number of chains can be large. There is no need to prepare a complex linking group with a large number of linking sites in order to prepare a many-branched star. Hence, in this aspect alone, the process of this invention provides significant improvement over the art.

In summary, this invention provides an efficient solution condensation process for the preparation of star polymers, which is not dependent on reactant stoichiometry. The method comprises a one-step functionalization which is very facile, when compared to -SiCl coupling chemistry. The molecular weight of the star product controls or substantially controls the shape of the star. The products are stable, isolatable, and soluble, and have inorganic and organic portions. The inorganic core or nucleus of the star has hydrophilic character and can enter into hydrogen bonding.

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The complexibility and molecular weight of the stars are dependent upon the heating temperature and the length of a heating period. Thus, stars having 4, 6, 10, 20, 30, or more arms can be readily prepared; however, the process can be stopped along the way to achieve isolatable stars of intermediate molecular weight.

The ability to prepare stars with a high number of arms, e.g., about 20, by a technique as simple as the process of this invention clearly shows the high degree of utility of the process and its patentability.

Compared to linear polymers of equivalent molecular weight, star polymers generally have decreased viscosity. Thus, the star polymers of this invention can be employed in those utilities where it is desirable to have a combination of high molecular weight and lower viscosity. For example, they can be employed in high solid contents coatings for rheological control. Furthermore, since the products of this invention have functional SiO_2 particles, they can be employed in paint and coatings applications. Furthermore, they can be used in other applications where it is desired to disperse SiO_2 or similar metal oxide particles. For example, they can be used to provide coatings with a controllable refractive index. The polymers of this invention can be used in hot melt adhesives.

The functionality, i.e., number of arms in the stellate polymers of this invention, can range from 2 to 20, 30, or more. A representative linked product of this invention has a molecular weight of about 4 times the molecular weight of said precursor. Products having a higher molecular weight compared to the precursor can be made by heating the precursor at a higher temperature and/or for a longer time.

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The temperature employed may be from ambient or slightly above ambient temperature to about 120°C or higher, preferably from about 30°C to about 120°C. Temperatures somewhat outside this range can be used.

5 The reaction time can be from about 3 hours to about two weeks. The process proceeds well at ambient pressure, but higher and lower pressures can be used.

As indicated above, this invention provides new compositions of matter; viz the polymeric products
10 produced by the above described process, utilizing either unfunctional or difunctional living polymers as starting materials.

Condensation products produced from silane endcapped, unfunctional polymers are preferred. They
15 are soluble in some common solvents, and therefore more easily tractable and characterizable than the analogous insoluble polymers made from silane-endcapped, alpha, omega difunctional living polymers.

The soluble polymers produced from endcapped,
20 unfunctional living polymers according to the process of this invention are characterized by having a narrow molecular weight distribution.

For the soluble condensation products, the ratio of the weight average molecular weight (M_w) to
25 the number average molecular weight (M_n), as depicted by the following relationship, is equal to a value within the range of from about 1.15 to about 1.70.

30
$$MWD = \frac{M_w}{M_n} \sim 1.15 - 1.70$$

The soluble condensates of this invention are therefore characterized by a Poisson (as opposed to a Gaussian) molecular weight distribution. In a
35 preferred embodiment, MWD is in the range of from about 1.20 to about 1.50.

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The starting materials (i.e. living polymers) from which the condensed products of this invention are produced have a narrow molecular weight distribution, as is characteristic of polymeric materials produced by an anionic polymerization. In contrast, the narrow molecular weight distribution of the condensed products of this invention is not wholly satisfactorily explainable, and was entirely unexpected.

10 As mentioned above, the soluble products of this invention comprise well defined stellate polymers with a discrete number of chains per polymer. It is believed that the insoluble products of this invention (which are produced from
15 difunctional living polymers) also have these characteristics, and also have a narrow molecular weight distribution similar to the soluble polymers discussed above.

Soluble, condensed polymers of this
20 invention can be employed to prepare protective films and coatings by applying them to substrates such as glass, plastic, or metal. The Si-OH groups already present in the polymers, or produced by reacting alkoxy groups with moisture after applying the
25 polymer to a substrate, adhere well to glass and other materials, thereby aiding formation of a protective coating or film.

The insoluble polymers of this invention can be incorporated into a suitable matrix and applied to
30 a substrate surface. Also, solutions of the difunctional precursor, water, and acid catalyst can be applied to a surface to be treated. After drying to remove excess water and solvent, the surface deposit can be heated to form a protective coating on
35 the substrate surface.

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Description of the Drawings

Figure 1 depicts an illustrative process of this invention. In the process, a "living" polystyrenyl lithium (produced by a living, anionic polymerization initiated with *sec*-butyl lithium) is
5 reacted with an endcapping agent. That agent is 90% by weight *p*-(chloromethylphenyl)trimethoxysilane, and 10% *o*-(chloromethylphenyl)trimethoxysilane. The endcapping reaction is conducted in tetrahydrofuran
10 (THF) at -78°C. The by-product (not shown) is lithium chloride.

As shown in the figure, the endcapped polymer is subsequently hydrolyzed in the presence of a catalytic quantity of HCl and condensed to yield a
15 product having an $\begin{array}{c} | \\ -\text{Si}-\text{O}-\text{Si}- \\ | \end{array}$ bridge.

Both silicon atoms in the condensed product are designated "T₁" silicons because each atom only participates in one Si-O-Si bond.

20 Although not shown in the figure, the condensed product can be further condensed with mild heating to form a structure having one or more "T₂" or "T₃" silicon atoms, i.e., silicon atoms which are bonded to two or three other silicon atoms via
25 oxygen linkages. Products containing one or more T₂ or T₃ silicons are discussed below.

For this invention, it is not necessary that all of the alkoxy groups (methoxy groups in the Figure) be hydrolyzed. In other words, there may be
30 some alkoxy groups and some hydroxy groups present.

The polystyrene living polymer used as a starting material in the process depicted in the figure is a unifunctional polymer, i.e., it has one metal cation. Difunctional living polymers, e.g.,
35 those having the general formula, M-P-M, wherein "M" is a monovalent metal cation and "P" is a

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difunctional living polymer, can also be reacted according to this invention. As discussed more fully below, difunctional condensed products are insoluble in a solvent such as THF, while the unfunctional
5 polymers remain soluble.

Figure 3 is a gel permeation chromatogram (a plot of concentration of polymer versus log molecular weight) of a ca. 3000 g/mole monofunctionalized polystyrene precursor (solid line) and a corresponding
10 condensate product of this invention. The condensate product was prepared as described herein and a film produced therefrom was heat treated at 75°C for 3 hours. The molecular weight of the product is approximately 4 times the precursor molecular
15 weight. In addition, the narrow molecular weight distribution of the condensate product suggests the formation of a well defined, star polymer.

Figure 2 is a ^{29}Si NMR spectrum of the condensate product depicted in Figure 3. The
20 chemical shifts are consistent with the formation of 60% T_2 silicon (approximately -68 ppm) and 40% T_1 (approximately -59ppm) silicon. The concentration of T_1 silicon is equivalent to the distance between lines (a) and (b) divided by the total distance
25 between lines (a) and (c). Similarly, the concentration of T_2 silicon is determined by the ratio of the distance between lines (b) and (c) divided by the distance between lines (a) and (c). There is generally less than 2% (unreacted precursor)
30 present after hydrolysis and condensation.

Best Mode For Carrying Out the Invention

This invention provides a process for the preparation of a polymer having a narrow molecular
35 weight distribution, said process comprising:

- (1) reacting a metal terminated anionic, living polymer with a halotrialkoxysilane wherein

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each alkoxy group has from 1 to about 4 carbon atoms to form a polymer endcapped with a trialkoxysilyl group, said process being conducted in the presence of an inert organic solvent for said metal terminated polymer;

(2) subjecting the trialkoxysilyl terminated polymer thereby produced to a hydrolysis/condensation reaction by contacting water with said trialkoxysilyl terminated polymer in the presence of a catalytic amount of an acidic or basic catalyst, and an inert organic solvent; and

(3) heating the precursor product thereby produced at a temperature and for a time sufficient to form a condensed polymer.

In a preferred embodiment, this invention provides a process comprising:

(a) reacting a metal terminated living anionic polymer with a silicon-containing endcapping agent;

(i) said metal terminated living polymer being selected from uni-functional and difunctional polymers having the respective formulas P-M and M-P-M, wherein M is a Group IA or Group IIA metal, and P is the anion of a living polymer of a conjugated diene or a vinyl substituted arene having up to about 18 carbon atoms, and

(ii) said silicon-containing endcapping agent has the formula $X-E_a-(CH_2)_n-Si(OR)_3$ wherein X is a halogen radical selected from fluoride, chloride, bromide, and iodide, E is a benzyl or substituted benzyl group having up to about 12 carbon atoms, such that said halogen

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radicals is bonded to the alpha carbon atom in said benzyl or substituted benzyl group, R is an alkyl radical of up to about 4 carbon atoms, a is equal to 0 or 1, and n is a whole number equal to 0 to 4,

to produce an endcapped functionalized polymer;

(b) subjecting said endcapped polymer to a hydrolysis/condensation reaction by contacting it with water in the presence of a catalytic quantity of an acid or base, and an inert organic solvent, to produce a polymer precursor;

(c) heating said polymer precursor at a temperature and for a time sufficient to form a condensed polymer wherein the ratio of T₁ silicon to T₂ silicon is 2:1 or lower.

The polymers of this invention have a narrow molecular weight distribution wherein MWD as defined above is equal to a value within the range of from about 1.15 to about 1.70. They comprise

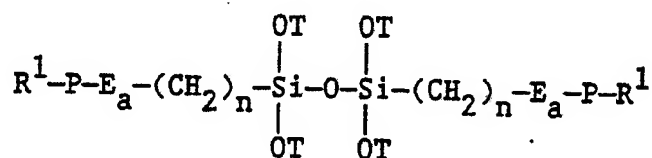
unifunctional or difunctional polymeric chains derived from living polymers made from dienes and/or vinyl substituted aromatics by an anionic polymerization.

In a preferred embodiment, this invention comprises a polymer having a MWD within the range of from about 1.15 to about 1.70, said polymer being selected from unifunctional and difunctional chains endcapped with a silicon-containing functionalizing group, said group being divalent and bonded through one valence to an end of said chain, and though the other valence to a silicon atom, which is bonded to three oxygen atoms, each of said oxygen atoms being

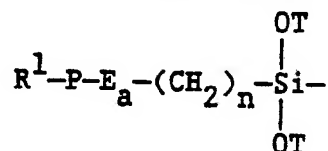
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bonded to a moiety selected from the hydrogen radical, lower alkyl radicals and another silicon (Si) in said chain, such that the ratio of the number of silicon atoms bonded to one other silicon atom via an oxygen bridge, to the number of silicon atoms bonded to two other silicon atoms via oxygen bridges is 2:1 or lower.

In a highly preferred embodiment, the polymers of this invention are soluble materials having the formula:



wherein E is a benzyl or lower alkyl substituted benzyl group having up to 12 carbon atoms, P is a poly(vinylaromatic) or poly(diene) chain wherein the individual vinylaromatic or diene groups in the chain have up to about 18 carbon atoms, R^1 is a lower alkyl (1-4 carbon atoms) or aryl group (10-14 carbon atoms) derived from the metal activator used in the preparation of the living polymer precursor, n is a whole number having a value of 0 to 4, a is equal to zero or 1, and T is selected from the hydrogen radical, alkyl radicals of from about one to about four carbon atoms, or the chain G, having the formula:



such that the ratio of the number of silicon atoms bonded to one other silicon atom via an oxygen bridge, (T_1 silicon) to the number of silicon atoms bonded to two other silicon atoms through oxygen bridges (T_2 silicon) is 2:1 or lower.

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Optionally, the polymers of this invention may have T_3 silicon atoms. In the soluble polymers of this invention, the relative number of T_3 silicon atoms compared to the total number of silicon atoms is quite low.

In the following relationship Si_{T_1} , Si_{T_2} and Si_{T_3} are respectively the number of T_1 , T_2 , and T_3 silicon atoms.

$$N\% = 100 \times \frac{Si_{T_3}}{[Si_{T_1} + Si_{T_2} + Si_{T_3}]}$$

For preferred products of this invention, N generally has a value of from about 0.0 to about 15%.

The metal terminated polymers used as starting materials in this invention have the formula P-M or M-P-M wherein P is a polymer chain and M is a metal of Group IA or IIA of the Periodic Table. Preferably the metal is magnesium, lithium or sodium; more preferably sodium or lithium.

The metal catalysts employed to form the metal terminated polymers can be organometallic compounds such as R-Li wherein R is a lower alkyl group of 2 to 8 carbons, e.g., butyl lithium. Sodium derivatives such as the sodium salts of α -methylstyrene, 1,1-diphenylethylene, naphthalene, and the like can also be employed as catalysts. Generally, 10^{-1} to 10^{-4} moles of catalyst are employed per each 100 grams of olefin.

Many unsaturated monomers containing carbon-to-carbon double bonds can be polymerized using metal catalysts to yield living polymers. These include conjugated and non-conjugated dienes and vinyl-substituted aromatic compounds. Some illustrative but non-limiting examples of useful

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dienes include the conjugated dienes having up to about 18 carbons, such as 1,3-butadiene, isoprene, 1,3-pentadiene, 2-phenyl-1,3-butadiene, 1,3-octadecene, and the like. Illustrative but non-limiting examples of vinyl substituted aryl monomers include styrene, 4-methylstyrene, 4-tert-butylstyrene, 4-decylstyrene, α -methylstyrene, 2-vinylnaphthalene, and other vinyl substituted aromatics having up to about 18 carbon atoms.

10 It will be understood by a skilled practitioner that the living polymers used as intermediates in this invention can be homopolymers, copolymers or block copolymers.

The living polymerization is conveniently carried out at a temperature of from about -85°C . to about 120°C . The polymerization is also conveniently carried out in a liquid ether or aliphatic hydrocarbon which does not react with the catalyst. Tetrahydrofuran, cyclohexane, petroleum ether, and the like can be used. (When a reaction medium, such as tetrahydrofuran, has a tendency to react with material(s) used in the process, such an undesirable side reaction can be minimized in some instances by conducting the process at a low temperature. Hence, one may use a reaction temperature as low as about -78°C when tetrahydrofuran is employed as the reaction medium).

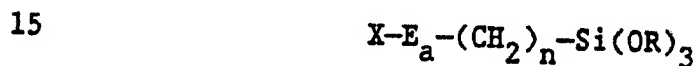
Further details concerning the preparation of living polymers of the type used in this invention are available in the art, e.g., U. S. Patents 3,956,419; 4,371,670; 4,379,891; 4,408,017; and 4,618,650. The descriptions of living polymers and methods for their formation within those patents are incorporated by reference herein as if fully set forth.

The process of this invention can be applied to living polymers having any molecular weight.

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However, as the molecular weight of the precursors increases, longer condensation times and/or higher temperatures are required. Although the molecular weight of the condensate influences the kinetics of the condensation, the formation of well-defined stellate polymers is independent of molecular weight. For convenience, it is preferred that the metal terminated polymer P-M or M-P-M have a polymeric chain with a molecular weight in the range of from about 500 to about 1,000,000, more preferably from about 1,000 to about 100,000.

After preparation, the living polymer is endcapped with a halo(alkoxy)silane having the formula



as described above. The efficiency of the functionalization using these endcapping agents can be followed by spectroscopic and chemical means even though the concentration of the end group is quite low.

The endcapping reaction can be carried out in the reaction medium in which the metal terminated polymer is formed. The reaction temperature is not critical. It has been conducted at -78°C in tetrahydrofuran and at 60°C in cyclohexane. Temperatures above and below those temperatures, e.g., from about -85°C to about 100°C , can be employed if desired.

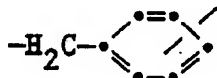
The endcapping reaction is preferably conducted using an excess (10-100 mole % or more) of the endcapping agent. However, it is not necessary that an excess be used; an exact stoichiometry can be employed, if desired.

Examples of the endcapping agents are triethoxychlorosilane and *p*-(chloromethylphenyl)trimethoxysilane. Such endcapping agents have an

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electrophilic site suitable for the deactivation of the polymeric anion.

When a in the above formula is equal to one, E is a group which activates the halogen X to make it reactable with the metal cation in the metal terminated polymer. Preferred endcapping groups comprise a benzyl radical;



10

A halogen is bonded to the carbon in the $-CH_2-$ group (the alpha carbon). The ring may be further substituted with groups which do not interfere in the reaction. In the endcapping agent, the depicted benzyl-type group is bonded to the $-Si(OR)_3$ moiety (directly or through an alkylene bridge) through the valence line shown. The alpha carbon atom may be ortho, meta, or para to the $Si(OR)_3$ moiety or bridging group. Other substituents such as lower alkyl groups illustrated by methyl, and ethyl and n-hexyl may be bonded to the ring.

Examples of endcapping agents useful in this invention are o-(chloromethylphenyl)trimethoxysilane, p-(chloromethylphenyl)trimethoxysilane, the triethoxy, tripropoxy, and tri-n-butoxy analogs of these compounds, o-(bromomethylphenyl)trimethoxysilane, p-(bromomethylphenyl)trimethoxysilane, 1-trimethoxysilyl-2-(p,m-chloromethyl)phenylethane, and the fluoro, and iodo analogs of those compounds. Compounds containing alkyl groups such as methyl, ethyl, and n-hexyl bonded to the ring are also useful. The endcapping agent may be a mixture of compounds; for example it may be a mixture of isomers such as 90% p-(chloromethylphenyl)trimethoxysilane and 10% by weight o-(chloromethylphenyl)-trimethoxysilane.

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In many instances, the reaction of the endcapping agent and the metal terminated polymer is quantitative or substantially quantitative. This maximizes the efficiency of subsequent incorporation
5 into a condensed polymer of this invention.

The functionalized polymers prepared by reacting the metal terminated polymers and above-described endcapping agents are soluble in a material such as tetrahydrofuran, dimethyl-
10 formamide, dimethylacetamide, acrylonitrile, N-methylpyrrolidone, sulfolane, dimethylsulfoxide, and the like.

Such solutions are admixed with an excess of water (compared to silicon) in order to hydrolyze and
15 condense the functionalized polymer.

The hydrolysis/condensation reaction is preferably conducted in the presence of an acid catalyst such as acetic acid or hydrochloric acid. Other volatile acids can be used. The acid can be
20 admixed with the water added to the solution or dispersions of the endcapped polymer. For example, the catalyst may be added as 0.15N HCl. Basic catalysts such as 1.0N NH_4OH can also be used.

The hydrolysis/condensation reaction is
25 conducted in general accordance with the art. Thus, it may be performed using conditions within the ranges set forth in Scholze et al, U. S. Patent 4,238,590 (col. 4, line 30, to col. 5, line 29). That portion of the Scholze patent is incorporated by
30 reference herein as if fully set forth.

Experimental

Materials and Purification

Styrene (Aldrich) and isoprene (Aldrich)
35 were stirred over finely ground calcium hydride for 1-2 days and vacuum distilled. The distilled monomers were stored at -25°C under nitrogen in a

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brown bottle until further use. Immediately prior to polymerization, the monomers were vacuum distilled from dibutyl magnesium (DBM). DBM (Lithco) was available as a 25% solution in heptane and transferred using syringe techniques. This reagent removes air and water from hydrocarbon monomers. The DBM was added dropwise to the monomer at room temperature until a stable, pale, yellow color persisted. It is believed that this color is associated with complexation of the unsaturated site and DBM. Typically, 60 mL of styrene required 4-5 mL of dibutyl magnesium. Both distillation yields were quantitative.

s-Butyllithium (s-BuLi) was obtained from Lithco Division of FMC as a 1.31M solution in hexane. The concentration of the solution was determined by the Gilman "double titration" technique and the homopolymerization of polystyrene. The initiator was generally used as received and was stored at -25°C for several months without significant degradation.

The sodium/naphthalene anion was utilized as the difunctional initiator. Naphthalene (scintillation grade, Aldrich) was sublimed at 30°C immediately prior to the initiator preparation. Sodium (Aldrich) was obtained as a neat chunk and used as received. Tetrahydrofuran (THF) was distilled from sodium/benzophenone under nitrogen immediately prior to the reaction. Approximately 1.5 g of sodium was finely sliced in a Schlenk vessel under a nitrogen purge. An equivalent weight of sublimed naphthalene was added to the sodium metal. The Schlenk vessel was capped with a rubber septum which was secured by copper wire and a positive pressure of nitrogen was maintained. Tetrahydrofuran (50 mL) was added via a syringe to the sodium/naphthalene at room temperature, and

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immediately a green color developed. The green color is indicative of the formation of the radical anion. The reaction was allowed to proceed for 18 hours, and the green solution was decanted with a cannula into a flame-dried bottle. The solution was generally used immediately; however, the radical anion was stored for later use at -25°C for 5-10 days.

Cyclohexane (Kodak, Reagent Grade) was stirred in the presence of concentrated sulfuric acid for 5-10 days to remove unsaturated impurities. The cyclohexane was decanted from the sulfuric acid and stirred over a sodium dispersion for several days. The solvent was distilled from the sodium dispersion under an argon atmosphere immediately prior to use. Tetrahydrofuran (Baker, HPLC Grade) was distilled from a purple sodium/benzophenone ketyl under argon immediately prior to polymerization.

p-(Chloromethylphenyl)trimethoxysilane (CMPTMS) (Petrarch) and triethoxychlorosilane (TECS) (Petrarch) were vacuum distilled immediately prior to use.

Polymerization

All glassware was rigorously cleaned and dried in an oven at 120°C for 24 hours. The reactor was a 250 mL, 1 neck, round-bottom flask equipped with a magnetic stirrer and a rubber septum. The septum was secured in place with copper wire in order that a positive pressure of ultra pure nitrogen could be maintained. The reactor was assembled while hot, and subsequently flamed under a nitrogen purge. After the flask had cooled, the polymerization solvent (tetrahydrofuran) was added to the reactor via a double-ended needle (cannula). The reactor was submerged into a -78°C bath and allowed to reach thermal equilibrium. Purified styrene monomer was charged into the reactor with a syringe. The calculated amount of initiator was quickly syringed

-20-

into the reactor and immediately one could see the formation of the orange polystyryl lithium anion. The polymerization was allowed to proceed for 20 minutes to ensure complete conversion.

5 Polymerizations were also conducted in cyclohexane using s-butyl lithium as the initiator. In this case, polymerizations were conducted at 60°C for two hours. The reactor consisted of a 3 neck, round-bottom flask which was fitted with an overhead
10 stirrer, a condenser, and a rubber septum. All reagents were added through the rubber septum. A nitrogen blanket was maintained throughout the polymerization.

15 Functionalization

Upon completion of the polymerization, the endcapping reagent (50% molar excess compared to lithium) was added quickly via a syringe. The complete disappearance of the orange color was
20 indicative of complete deactivation of the polymeric carbanion.

The functionalization, i.e. endcapping, reaction can be conducted at a temperature of from about -85°C. to about 100°C. Temperatures somewhat
25 outside this range can also be used. The reaction pressure can be about ambient, preferably in the range of from about atmospheric pressure to about 10 psig. When the endcapping group contains a benzyl radical as discussed above, the reaction time is in
30 the order of about one-half an hour. When an endcapping group such as $X-Si(OR)_3$ wherein is used (X is halogen, and R is an alkyl group of 1-4 carbon atoms), a somewhat longer reaction time of from about 1.5 to about 3.0 hours is employed.

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Polymer Purification

After functionalization, the polymers (molecular weights greater than 3000 g/mole) were precipitated in HPLC grade methanol which contained < 0.05% water (determined by titration). The precipitation and vacuum filtration were conducted under a nitrogen blanket to minimize hydrolysis of the trialkoxysilyl end groups.

Polymers which had molecular weights below 3000 g/mole were not precipitated in order to avoid fractionation. Such low molecular weight polystyrenes were soluble in methanol.

The polymerization solvent was removed by rotoevaporation. All samples were dried in vacuo at 80°C. for 12-18 hours.

Characterization

Molecular weights and molecular weight distributions of the endcapped (i.e. functionalized) polymers were determined by Size Exclusion Chromatography (SEC) in THF at 25°C. A variable temperature Waters GPC was equipped with ultrastyrigel columns of 10^3 Å, 500 Å, and 100 Å for molecular weights less than 5000 g/mole, and 10^6 Å, 10^5 Å, 10^4 Å, and 10^3 Å for higher molecular weights. A Waters Differential Refractive Index (DRI) was utilized. Polystyrene standards (Polymer Laboratories) were used for the construction of calibration curves. The hydrolyzed/condensed, monofunctional polymers were also analyzed by SEC using a viscometric detector to obtain absolute molecular weights and to determine the extent of condensation.

¹H Nuclear Magnetic Resonance characterization was accomplished using a General Electric QE300 300 MHz NMR Spectrometer. The instrument was equipped with a superconducting magnet

-22-

and had a 7.05T field strength. The spectrometer was run by a Nicolet 1280 computer and the frequency resolution was 1.2 Hz. All samples were referenced to CHCl_3 .

5 As discussed above the reaction of "living" polystyryl lithium with p-(chloromethylphenyl)tri-methoxysilane is depicted in Figure 1. The orange color which is associated with the polystyryl lithium carbanion disappears immediately upon addition of the
10 endcapping reagent. ^1H NMR analysis indicates the presence of the trialkoxysilyl group at 3.6 ppm. The presence of the initiator fragment which resides at the other end of the polymer chain is also evident between 0.6 and 1.2 ppm. Either the initiator fragment or the
15 trialkoxysilyl group integration was compared to the repeat unit methylene and methine integration in order to determine functional molecular weights.

Table 1 (below) shows the functional molecular weights for various endcapped polystyrene samples.
20 Excellent agreement exists between the molecular weights based on the initiator fragment and molecular weights based on the trialkoxysilyl end group. In addition, the functional molecular weights compare favorable with the number average molecular weights
25 determined by Size Exclusion Chromatography (SEC). These observations demonstrate an efficient and quantitative endcapping reaction. Molecular weight distributions are also fairly narrow (1.10-1.20) which indicate a well-defined polymerization and efficient
30 functionalization reaction. The preparation of very narrow (<1.1) polydispersity, low molecular weight polymers is difficult in polar solvents due to comparable rates of initiation and propagation.

Table 1

5 Molecular Weight Determinations For p-(Chloromethyl-phenyl)trimethoxysilane Terminated Polystyrene Polymers

	<u>Sample</u> ^a	<u>Mn(GPC)</u> ^b	<u>Mn(NMR)</u> ^c	<u>Mn(NMR)</u> ^d	<u>Mw/Mn</u>
	-Si(OCH ₃) ₃				
10	7202-35	3,900	3,000	3,100	1.19
	7202-44B	3,100	2,700	2,700	1.13
	7202-97C	3,900	3,500	3,500	1.22

15 ^a Polymerization Conditions: THF, -78°C, s-Butyl-lithium

^b Polystyrene Standards, THF, 25°C, DRI Detector

20 ^c Ratio repeat unit resonance to initiator fragment (s-butyl)

^d Ratio repeat unit resonance to Si(OR)₃

25 ²⁹Si spectra were obtained with a Bruker AM-500 instrument at 99.32 MHz. All samples were referenced to tetramethylsilane (TMS). Chromium acetylacetonate [Cr(AcAc)₃] was added at approximately 0.015M to reduce the longitudinal relaxation time (T₁) for the silicon-29 spectra.

30 The silicon-29 spectra were obtained using inverse-gated decoupling (decoupler on during acquisition and off during the relaxation delay) to suppress any negative nuclear Overhauser effect. The relaxation agent and decoupling sequence facilitated

35 quantitative measurements.

The glass transition temperatures of the endcapped and the hydrolyzed/condensed polymers were

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determined with a Perkin Elmer Differential Scanning Calorimeter (DSC) System 2. The first run was heated to 200° at 20°C per minute and quenched. The glass transition was determined on the second run at 20°C per minute.

Neutron Activation Analysis (NAA) also was utilized to verify the presence of both silicon and oxygen in the polymer and to calculate functional molecular weights. Functional molecular weights were obtained by comparing the percent silicon or oxygen to the percent carbon. Table 2 lists the functional molecular weights determined by both NMR and NAA for two samples. Excellent agreement exists between the different analyses.

Table 2

Molecular Weight Determinations By Neutron Activation Analysis (NAA) for CMPTMS Terminated Polystyrene Polymers

Sample ^a	Mn(NMR) ^b	Mn(NMR) ^c	Mn(Si)	Mw(O)
-Si(OCH ₃) ₃				
7202-44B	2,700	2,700	2,600	2,700
7202-35	3,000	3,100	3,100	3,300

- ^a Mn(theoretical) = 2,800 g/mole
^b Based on initiator fragment (s-butyl)
^c Based on Si(OR)₃

²⁹Si NMR is a discriminatory technique for the characterization of the endcapped polymers. In most cases, a resonance which is associated with a trimethoxysilyl group is only observed at approximately -54 ppm. However, hydrolysis and condensation of the end groups during either precipitation or in air often lead to a small amount (2-10%) of dimer formation. The dimer Si-O-Si resonance appears at approximately -65 ppm. ²⁹Si

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NMR also confirms that displacement of the methoxy group during functionalization does not occur.

Similar functionalized polymers were obtained using triethoxychlorosilane as the functionalization agent. The molecular weight determinations for such materials are set forth in Table 3.

Table 3

10 Molecular Weight Determinations For Triethoxychlorosilane (TECS) Terminated Polystyrene Polymers

	<u>Sample^a</u>	<u>Mn(GPC)^b</u>	<u>Mn(NMR)^c</u>	<u>Mn(NMR)^d</u>	<u>Mw/Mn</u>
15	-Si(OCH ₂ CH ₃) ₃				
	7202-73B	4,300	4,000	4,000	1.15
	7202-73D	3,500	3,400	3,000	1.13
	7202-63A	4,600	4,000	4,000	1.11

- 20 ^a Polymerization Conditions: THF, -78°C, s-Butyl-lithium
- ^b Polystyrene standards, THF, 25°C, DRI Detector
- ^c Ratio repeat unit resonance to initiator fragment (s-butyl)
- 25 ^d Ratio repeat unit resonance to Si(OR)₃

Hydrolysis and Condensation

The polymers were dissolved in tetrahydrofuran (15-18% solids), and a 4:1 molar ratio of water compared to silicon (based on polymer repeat unit molecular weight) was added as a 0.15 N solution of HCl. The solutions were allowed to evaporate slowly at room temperature for 4 days. The resulting films were dried in vacuo at various conditions.

After allowing the solutions to dry to a film in air, the samples were heated in vacuo at

-26-

various conditions. Variables such as trialkoxysilyl group, molecular weight, functionality, and subsequent heat treatment were addressed.

Table 4 describes the change in the glass transition temperature (T_g) of the functionalized polystyrene polymers upon hydrolysis and condensation.

10

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Table 4

Effect of Hydrolysis and Condensation on the Glass Transition Temperature of Functionalized Polystyrene Polymers

Sample ^a	End Group	Conditions	Functionality	T _g (°C) ^b	ΔC _p ^c
44BB	Si(OCH ₃) ₃	ACID	1	72	0.27
44BA			1	84	0.18
97CB	Si(OCH ₃) ₃	ACID	1	78	0.30
97CA			1	89	0.21
73CB	Si(OCH ₂ CH ₃) ₃	ACID	1	84	0.22
73CA			1	83	0.22
112BB	Si(OCH ₃) ₃	ACID	2	96	0.30
112BA			2	101	0.28
NBS PS	H		0	102	0.31

^a Reactions in THF at room temperature

^b Heating Rate: 20°C/min., Nitrogen

First Scan: 25°C to 200°C; T_g determined on second scan

^c J / g • K

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In each case, the samples were dried in vacuo at 75°C for 3 hours prior to DSC analysis. The Tg was determined on the second run. The first run was heated to 200°C and quenched; this ensured the removal of residual THF and water. A sample which was not treated with acid and water was designated by B (Blank) as the final letter in the sample name. If the sample was hydrolyzed/condensed with acid and water, then an A (Acid) was added as the final letter as the sample name. Samples 44B (2800 g/mole) and 97B (5000 g/mole) were both terminated at one end with a trimethoxysilyl group. Sample 112B (26,000 g/mole) was terminated at both ends with trimethoxysilyl groups, and sample 73C (5000 g/mole) was terminated at one end with a triethoxysilyl group.

In all cases, the Tg (glass transition temperature) of the trimethoxysilyl terminated polymers increased upon hydrolysis and condensation; however, the Tg of the triethoxysilyl terminated oligomer did not increase under the same conditions. This implies that the triethoxysilyl group is less reactive than the trimethoxysilyl at the same conditions and condensation does not occur unless more rigorous conditions are used. The increase in Tg is associated with the increase in the molecular weight of the polystyrene; however, the presence of SiO₂ linkages may also contribute to an increase in the Tg.

The solubility characteristics of the hydrolyzed/condensed, trimethoxysilyl terminated polystyrene polymers are of particular interest. After the hydrolysis and condensation of the monofunctionally terminated polymers, the films remained soluble in tetrahydrofuran. This characteristic facilitates the characterization of the reaction product by spectroscopic and gel

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permeation chromatographic techniques. The difunctional polymers were rendered insoluble after the hydrolysis and condensation. The films would only swell in tetrahydrofuran.

5 The solubility of the monofunctional condensates permits the facile characterization of the hydrolysis and condensation reactions. This is very difficult for difunctional (telechelic) condensates.

10 A Size Exclusion Chromatograph which was equipped with a viscometric detector was utilized to determine absolute molecular weight changes after hydrolysis and condensation. Fig. 3 depicts the chromatograms of the unreacted, trimethoxysilyl
15 terminated precursor (solid line) and the product of the hydrolysis/condensation after heating at 75°C for 3 hours (dashed line). A striking feature is the narrow molecular weight distribution of the condensate. The weight average molecular weight of
20 the condensate is approximately four times the molecular weight of the precursor. This implies that a well defined macromolecule with four branches, a star or stellate polymer, was efficiently formed under these conditions; however, the processing
25 conditions define the size of the condensate. The absence of appreciable, uncondensed precursor in the chromatogram of the condensate implies that the endcapping reaction was quite efficient. This type of behavior was reproducibly observed for various
30 trimethoxysilyl terminated precursors which had different molecular weights. However, as the molecular weight increased, the films were generally heated above T_g (120°C. for polystyrene) for 3-5 days in order to promote condensation in the solid state.
35 Hydrolysis and condensation of the triethoxysilyl terminated polystyrene polymers demonstrated similar condensation behavior.

-30-

The increase in molecular weight upon hydrolysis and condensation was also confirmed by intrinsic viscosity measurements. Table 5 depicts two samples which have different precursor weight average molecular weights and the corresponding condensates. Both precursors were anionic living poly(styrenyl) polymers quantitatively monofunctionalized with CMPTMS, condensed, and heat treated in the solid state for 3 hours at 75°C. as described earlier. In each case, the intrinsic viscosity of the condensate was higher than the intrinsic viscosity of the precursor. This observation was consistent with an increase in the weight average molecular weight determined by gel permeation chromatography (GPC).

Table 5

Sample	Mw	[η]	a	log K
Precursor	5000	0.062	0.640	-3.53
Condensate	20200	0.092	0.604	-3.60
Precursor	2800	0.047	0.660	-3.509
Condensate	17600	0.070	0.608	-3.699

The intrinsic viscosity [η] of the resultant condensates was lower than the viscosity for a corresponding linear polymer which had an equivalent molecular weight. The ratio of the condensate viscosity to the linear polymer viscosity is defined as g, and values less than one indicate that the macromolecule has a branched topology. This value was substituted into the Zimm Equation and the number of branches was determined (Zimm f). In addition, the condensate molecular weight (GPC) was compared to

-31-

the precursor molecular weight (GPC) to determine the number of branches. Table 6 depicts the results for the condensates shown in Table 5.

5

Table 6

	<u>Condensate Mw</u>	<u>G</u>	<u>Zimm f</u>	<u>GPC f</u>
10	20,200	0.628	4	4
	17,600	0.528	5	6.3

The a values given in Table 5 are derived from the Mark-Houwink relationship. A decreasing "a" value is also indicative of a branched structure. Since the condensation reactions are only occurring at the polymer chain ends, it appears that the branched condensate is a star (i.e. stellate) polymer.

As mentioned above, the molecular weight of the precursor alters the kinetics of the condensation reaction in the solid state. Table 7 describes the effect of precursor molecular weight on the molecular weight of the condensate. In each case, the condensates were vacuum dried at 70°C. for 3 hours. The intrinsic viscosities also increase upon condensation. The GPC functionality (f) is also shown for each condensate. By comparing the precursor molecular weight values with the values for "f", it is clear that as the molecular weight of the precursor increases, the growth becomes more difficult at similar processing conditions. This effect is believed to be a function of the glass transition temperature of the precursor and condensate relative to the processing temperature.

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Table 7

	Precursor	Precursor	Condensate	Condensate	
5	<u>Mw</u>	<u>[n]</u>	<u>Mw</u>	<u>[n]</u>	<u>f</u>
	2,800	0.047	17,600	0.070	6.2
	5,000	0.062	20,200	0.092	4.0
	12,200	0.115	45,700	0.177	3.7
10	35,300	0.219	95,300	0.311	2.7

Table 8 describes the effect of processing conditions on the molecular weight of the unifunctional condensed products. At each stage of the process, the condensates are readily soluble in common organic solvents such as THF and are amenable to GPC analysis. The growth of the condensates gradually decreases and a finite functionality is ultimately obtained. For the sample described in Table 8 the ultimate number of branches is 6.1.

Table 8

	<u>Sample Conditions</u>	<u>Mw</u>	<u>Mw/Mn</u>	<u>[n]</u>	<u>f</u>
25	Precursor	35,300	1.14	0.219	1
	Cast Film Air Dried at 25°C.	87,500	1.33	0.315	2.5
	Cast Film Above and 3 hrs.. at 75°C.	95,300	1.33	0.311	2.7
30	Cast Film Above and 19 hrs.. at 120°C.	163,000	1.44	0.371	4.6
	Cast Film Above and 72 hrs.. at 120°C.	214,000	1.44	0.375	6.1

In the above Table, third entry first column, the term "Cast Film Above and 3 hours at 75°C." means that the cast film dried at 25°C. (second entry in

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column 1) was heated for an additional 3 hours at 75°C. Thereafter, the film was then heated for 19 hours at 120°C., (fourth entry) and then for an additional 72 hours at 120°C. (fifth entry). The molecular weight, intrinsic viscosity and functionality data reported in the table were ascertained as shown, at each point in this step-wise process.

Due to the decreased reactivity of the triethoxysilyl functionality compared to trimethoxysilyl, longer hydrolysis times (5-10 days) at high temperatures are required to obtain similar condensation products.

Monofunctional condensates were analyzed by ^{29}Si NMR in solution. The spectrum in Fig. 2 implies that two different types of silicon (60:40) are present in the branched molecule. The chemical shifts are consistent with 60% T_2 and 40% T_1 . This spectrum was identical for two different molecular weight precursors (2800 and 5000 g/mole) which were treated in a similar fashion. This analysis implies that the condensate is not a single, cyclic species unless rapid equilibration is occurring. Consequently it is believed the condensate simply consists of a linear silicon-oxygen backbone with pendant polystyrene branches.

As mentioned earlier, the difunctional condensates were insoluble and not amenable to SEC analysis.

The number of arms was drastically increased by longer processing times at 120°C. Table 9 depicts various precursor (arm) molecular weights and the condensate molecular weights after processing at 120°C for 240 hours. As stated earlier, the precursor molecular weight controls the kinetics of condensation, and lower molecular weight precursors generally lead to more branched products. In fact, the 2100 g/mole and

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3900 g/mole precursors resulted in 17.0 and 15.6 arm star polymers respectively. It is important to note that the molecular weight distribution of the condensed product remains relatively narrow as described earlier (1.15-1.70). Once again, the number of arms was estimated by dividing the condensate peak molecular weight as determined by GPC by the precursor number average molecular weight. The condensates eventually stopped increasing in molecular weight, and an equilibrium number of arms was obtained. The exact number of arms is a function of the processing conditions, and various branched condensates were isolated throughout the process. A skilled practitioner can alter the solution or solid state processing conditions to achieve different numbers of arms in the condensate. For example, longer reaction periods at higher temperatures can produce products with more star arms, e.g., 20, 30, or more.

20

Table 9

Effect of Precursor Molecular Weight On Star Growth at 120°C/240 Hours

25	<u>Precursor Mn</u>	<u>Condensate Mp</u>	<u>Number of Arms</u>
	2,100	35,100	17.0
	3,700	56,600	15.5
	8,400	84,200	10.0
	49,800	137,000	2.7

30

A skilled practitioner, familiar with the above-detailed description of the process and products and utilities of this invention, can make many substitutions and changes without departing from the scope and content of the appended claims.

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Claims:

1. Process for the preparation of a polymer having a narrow molecular weight distribution, said process comprising:
 - 5 (i) reacting a metal terminated living anionic polymer with a halotrialkoxysilane wherein each alkoxy group has from one to about four carbon atoms and to form a polymer endcapped with a trialkoxysilyl group, said process being
10 conducted in the presence of an inert organic solvent for said metal terminated polymer,
 - (ii) subjecting the trialkoxysilyl terminated polymer thereby produced to a hydrolysis/condensation reaction by contacting
15 water with said trialkoxysilyl terminated polymer in the presence of a catalytic amount of an acidic or basic catalyst, and an inert organic solvent,
 - 20 (iii) heating the precursor product thereby produced at a temperature and for a time sufficient to form a condensed polymer.
2. Process of Claim 1 wherein step (i) is
25 conducted at about ambient temperature.
3. Process of Claim 1 wherein step (ii) is
conducted at about ambient temperature.
4. Process of Claim 2 wherein step (ii) is
30 conducted at about ambient temperature.
5. Process for the preparation of a polymer having a narrow molecular weight distribution, said process comprising:
 - 35 (a) reacting a metal terminated living anionic polymer with a silicon-containing endcapping agent,

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- (i) said metal terminated living, anionic polymer being selected from unifunctional and difunctional polymers having the respective formulas P-M and M-P-M, wherein M is a Group Ia or Group IIa metal and P is the anion of a living polymer of a conjugated diene or a vinyl substituted arene having up to about 18 carbon atoms, and
- (ii) said silicon-containing, endcapping agent has the formula $X-E_a-(CH_2)_n-Si(OR)_3$ wherein X is a halogen radical selected from fluoride, chloride, bromide, and iodide, E is a benzyl or substituted benzyl group having up to about 12 carbon atoms such that said halogen radical is bonded to the alpha carbon atom, in said benzyl or substituted benzyl group, R is an alkyl radical of up to about 4 carbon atoms, n is a whole number equal to zero to 4, and a is equal to 0 or 1, to produce an endcapped functionalized polymer;
- (b) subjecting said functional polymer to a hydrolysis/condensation reaction by contacting it with water in the presence of a catalytic quantity of an acid or base, and an inert organic solvent, to produce a polymer precursor;
- (c) heating said polymer precursor at a temperature and for a time sufficient to form a condensed polymer wherein the ratio of T_1 silicon to T_2 silicon is 2:1 or lower.

6. Process of Claim 5 wherein the solvent/polymer precursor product of step (b) is dried under ambient conditions to form a film of said precursor, and step (c) is conducted using said film.

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7. Process of Claim 6 wherein each R is methoxy.

8. Process of Claim 7 wherein said endcapping agent is p-(chloromethylphenyl)tri-methoxysilane.

9. Process of Claim 5 wherein step (c) is conducted at a temperature of from about 60°C to about 120°C for a time of from about 2 hours to about 5 days.

10. Process for the preparation of a condensed polymer having a narrow molecular weight distribution, said process comprising:

(a) subjecting a living anionic polymer terminated with a tri(lower alkyl) silyl group to a hydrolysis/condensation reaction, by contacting said terminated polymer with water in the presence of an acid or basic catalyst and an organic solvent for said terminated polymer,

(b) heating the solvent/precursor mixture thereby produced at a mild temperature and for a time sufficient to produce a condensed product having a molecular weight of about 4 times the molecular weight of said precursor.

11. Process of Claim 10 wherein said living polymer substantially consists of repeating units formed from a conjugated diene.

12. Process of Claim 11 wherein said living polymer is polyisoprene.

13. Process of Claim 10 wherein said living polymer is polystyrene.

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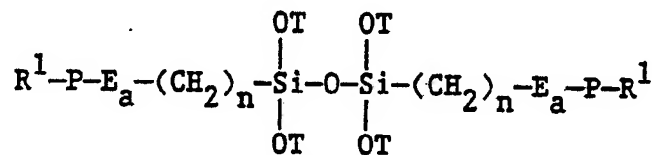
14. Process of Claim 10 wherein said terminating group is the tri(ethoxy)silyl radical.

15. Process of Claim 10 wherein said terminating group is the *o* or *p*-(chloromethyl-phenyl)trimethoxysilyl radical.

16. Process of Claim 1 wherein said solvent employed in step (a) is selected from the class consisting of ethers and hydrocarbons having a normal boiling point of up to about 110°C.

17. A polymer having a MWD within the range of from about 1.15 to about 1.70, said polymer being selected from unifunctional and difunctional chains endcapped with a silicon-containing functionalizing group, said group being divalent and bonded through one valence to an end of said chain, and through the other valence to a silicon atom, which is bonded to three oxygen atoms, each of said oxygen atoms being bonded to a moiety selected from the hydrogen radical, lower alkyl radicals and another silicon atom of said chain, such that the ratio of the number of silicon atoms bonded to one other silicon atom via an oxygen bridge, to the number of silicon atoms bonded to two other silicon atoms via oxygen bridges is 2:1 or lower.

18. Soluble polymers having the formula.



wherein E is a benzyl or lower alkyl substituted benzyl group having up to 12 carbon atoms, P is a

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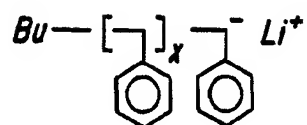
poly(vinylaromatic) or poly(diene) wherein the vinylaromatic or diene groups have up to about 18 carbon atoms, R^1 is a lower alkyl (1-4 carbon atoms) or aryl group (10-14 carbon atoms) derived from the metal activator used in the preparation of the living polymer precursor, n is a whole number having a value of 1-4, a is equal to zero or 1 and T is selected from H, R, or another silicon of said chain such that the ratio of the number of silicon atoms bonded to one other silicon atom via oxygen bridges, (T_1 silicon) to the number of silicon atoms bonded to two other silicon atoms through oxygen bridges (T_2 silicon) is 2:1 or lower, and such that the MWD of said polymer is within the range of from about 1.15 to about 1.70.

19. The chain of Claim 18 wherein P is selected from poly(vinylaromatic) and poly(diene) moieties having a molecular weight of from about 500 to about 1,000,000.

20. The polymer of Claim 19 wherein P is a poly(vinylaromatic).

21. The polymer of Claim 20 wherein P is poly(styrene).

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*Bu* = *s*-butyl

+

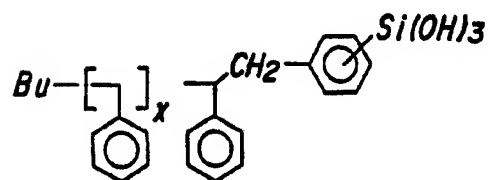
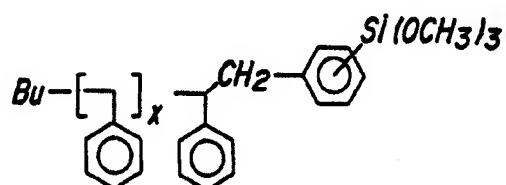
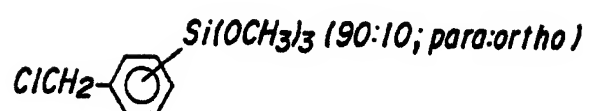
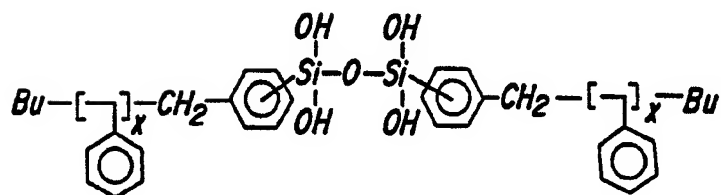
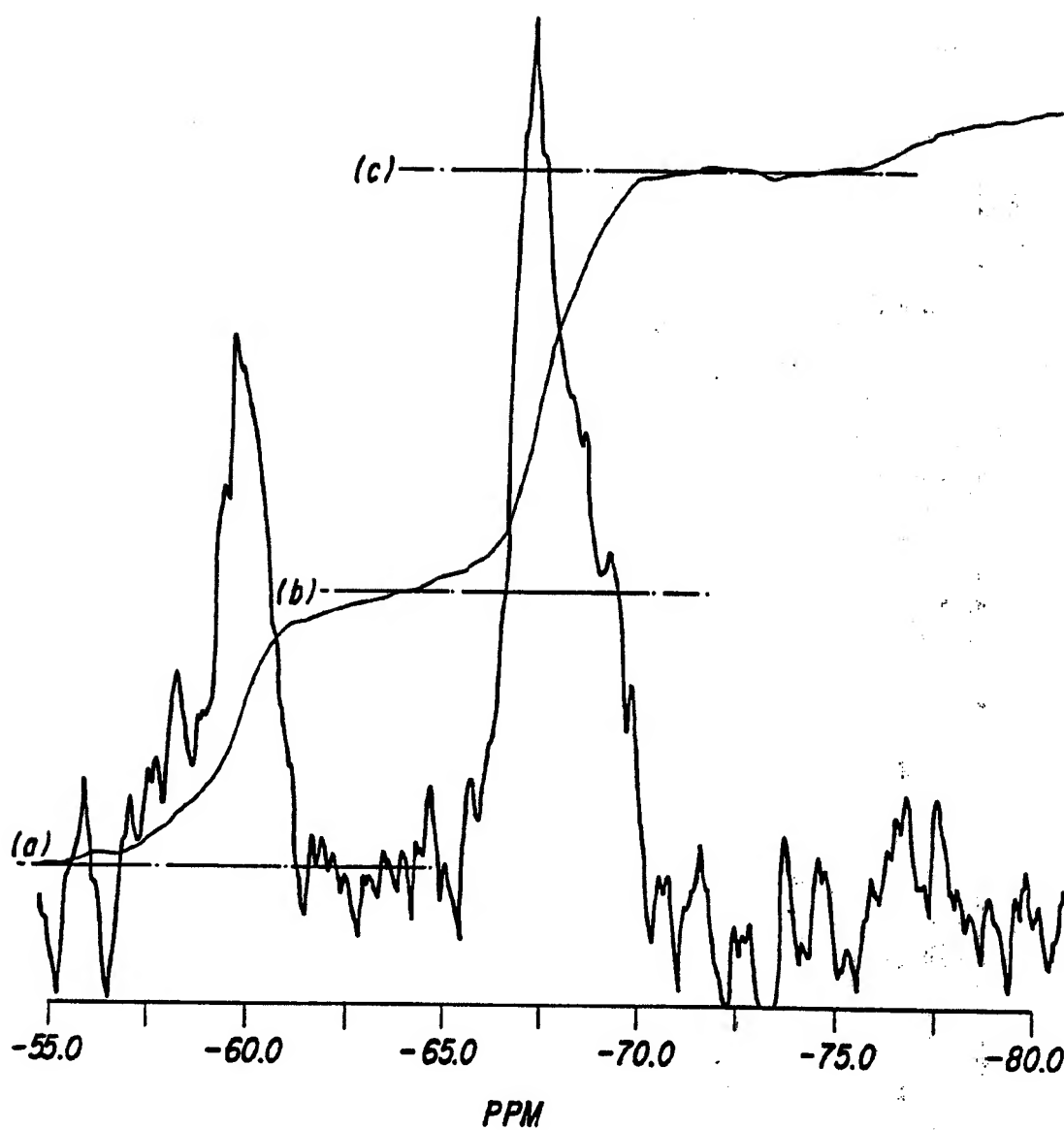
+ 3 CH₃OH

FIG. 1

2/3

**FIG. 2**

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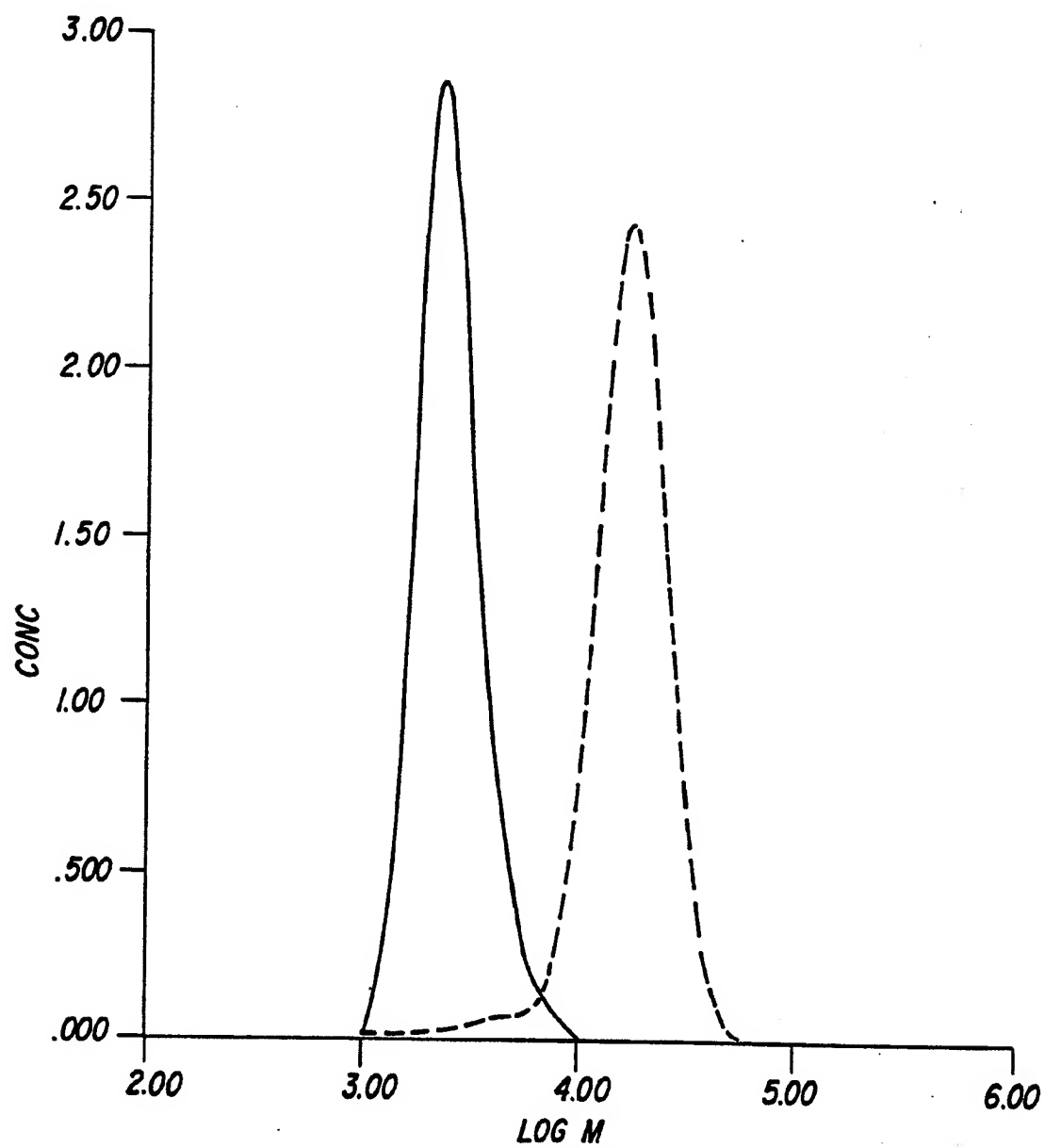


FIG. 3

INTERNATIONAL SEARCH REPORT

International Application No PCT/US 90/00760

I. CLASSIFICATION OF SUBJECT MATTER (if several classification symbols apply, indicate all) ⁶ According to International Patent Classification (IPC) or to both National Classification and IPC IPC5: C 08 F 297/02, C 08 F 8/42, C 08 G 81/02, C 08 C 19/44		
II. FIELDS SEARCHED		
Minimum Documentation Searched ⁷		
Classification System	Classification Symbols	
IPC5	C 08 F; C 08 G; C 08 C	
Documentation Searched other than Minimum Documentation to the Extent that such Documents are Included in Fields Searched ⁸		
III. DOCUMENTS CONSIDERED TO BE RELEVANT⁹		
Category [*]	Citation of Document, ¹¹ with indication, where appropriate, of the relevant passages ¹²	Relevant to Claim No. ¹³
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* Special categories of cited documents:¹⁰ "A" document defining the general state of the art which is not considered to be of particular relevance "E" earlier document but published on or after the international filing date "L" document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified) "O" document referring to an oral disclosure, use, exhibition or other means "P" document published prior to the international filing date but later than the priority date claimed "T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention "X" document of particular relevance, the claimed invention cannot be considered novel or cannot be considered to involve an inventive step "Y" document of particular relevance, the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art. "&" document member of the same patent family		
IV. CERTIFICATION		
Date of the Actual Completion of the International Search 15th May 1990		Date of Mailing of this International Search Report 0 6. 05. 90
International Searching Authority EUROPEAN PATENT OFFICE		Signature of Authorized Officer H. Daniels

III. DOCUMENTS CONSIDERED TO BE RELEVANT (CONTINUED FROM THE SECOND SHEET)		
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**ANNEX TO THE INTERNATIONAL SEARCH REPORT
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SA 34600

This annex lists the patent family members relating to the patent documents cited in the above-mentioned international search report.
The members are as contained in the European Patent Office EDP file on 07/05/90
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